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(54) An optical element having cured coating film

(57) The invention provides a cured film-coated optical element having good scratch resistance, good moisture resistance and good weather resistance, of which the properties are degraded little even when it is further coated with a deposit film of an inorganic oxide. Provided is an optical element having, on an optical substrate, a cured film formed of a coating agent that contains (A) modified stannic oxide-zirconium oxide composite colloid particles as prepared by coating at least a part of the surfaces of stannic oxide-zirconium oxide composite colloid particles with stannic oxide-tungsten oxide-silicon oxide composite colloid particles, and (B) an organosilicon compound.

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Description

[Technical Field to which the Invention Belongs]

[0001] The present invention relates to an optical element having a cured coating film, more precisely, to an optical element having a cured coating film (this will be simply referred to as a cured film), which has good scratch resistance, good moisture resistance and good weather resistance and of which the properties are degraded little even when it is further coated with a deposit film of an inorganic oxide.

[Prior Art]

[0002] Heretofore in general, for making plastic moldings having scratch resistance, a method of providing a coating film with scratch resistance on its surfaces is employed. As coating compositions to be used for forming such a coating film, for example, proposed are coating compositions containing a colloidally-dispersed silica sol (Japanese Patent Laid-Open No. 111336/1978), a coating composition containing fine tin oxide particles coated with fine tungsten oxide particles (Japanese Patent Laid-Open No. 172369/1991), a coating composition containing a sol of tin oxide colloid particles modified with tin oxide-tungsten composite colloid particles (Japanese Patent Laid-Open No. 25603/1994), etc.

[0003] However, these coating compositions are all problematic in that, when they are coated, for example, on optical substrates, they could not form coating films thereon capable of making the coated substrates having good scratch resistance and good moisture resistance while naturally having esthetic appearances (this means that the coated substrates do not form interference fringes to be caused by the difference in the refractive index between the coating film and the substrate) and good weather resistance, and that, even when a deposit film is further provided thereon, the coated substrates could not still have satisfactory scratch resistance and satisfactory moisture resistance while naturally having esthetic appearances and good weather resistance.

[Problems that the Invention is to Solve]

[0004] In that situation, the object of the present invention is to solve the problems with the prior art and to provide an optical element having a cured film, which has good esthetic appearances, good weather resistance, good scratch resistance and good moisture resistance and of which the properties are degraded little even when it is further coated with a deposit film.

[Means for Solving the Problems]

[0005] We, the present inventors, have developed an optical element having a cured film and having good properties as above, and, as a result, have found that, when a coating composition containing specific modified stannic oxide-zirconium oxide composite colloid particles and an organosilicon compound is coated on an optical substrate to form a cured film thereon, then the object can be attained. On the basis of this finding, we have completed the invention.

[0006] Specifically, the invention provides an optical element having a cured film on an optical substrate, which is characterized in that the cured film is formed of a coating agent containing (A) modified stannic oxide-zirconium oxide composite colloid particles as prepared by coating at least a part of the surfaces of stannic oxide-zirconium oxide composite colloid particles with stannic oxide-tungsten oxide-silicon oxide composite colloid particles, and (B) an organosilicon compound.

[Modes of Carrying out the Invention]

[0007] The optical element having a cured film of the invention (this will be hereinafter simply referred to as "optical element of the invention") comprises an optical substrate and a cured film of a specific coating agent provided thereon, and the coating agent contains modified stannic oxide-zirconium oxide composite colloid particles as the component (A), and an organosilicon compound as the component (B).

[0008] The modified stannic oxide-zirconium oxide composite colloid particles of the component (A) are prepared by coating (α) a part or all of the surfaces of stannic oxide-zirconium oxide composite colloid particles with (β) stannic oxide-tungsten oxide-silicon oxide composite colloid particles. The colloid particles of the component (α) are to be the nuclei of the modified stannic oxide-zirconium oxide composite colloid particles. Preferably, these are composed of stannic oxide colloid particles and zirconium oxide colloid particles bonded in a ratio by weight, ZrO_2/SnO_2 falling between 0.02 and 1.0, and have a particle size of from 4 to 50 nm, in view of the properties of the coating agent to be prepared herein.

[0009] On the other hand, also preferably, the stannic oxide-tungsten oxide-silicon oxide composite colloid particles

of the component (β) which are to coat a part or all of the surfaces of the colloid particles of the component (α) have a ratio by weight, WO_3/SnO_2 and a ratio by weight, SiO_2/SnO_2 each falling between 0.1 and 100, and have a particle size of from 2 to 7 nm, more preferably from 2 to 5 nm, in view of the properties of the coating agent to be prepared herein.

[0010] In view of the stability and the properties of the coating agent containing them, the modified stannic oxide-zirconium oxide composite colloid particles of the component (A) preferably have a particle size of from 4.5 to 60 nm.

[0011] In the invention, the modified stannic oxide-zirconium oxide composite colloid particles of the component (A) can be efficiently prepared, for example, according to a process comprising the following steps (a), (b), (c), (d) and (e).

<u>Step (a)</u>:

[0012] Step (a) is to mix an aqueous stannic oxide sol with an aqueous solution or suspension of an oxyzirconium salt. Preferably, the aqueous stannic oxide sol contains stannic oxide colloid particles having a particle size of from 4 to 50 nm, and has an SnO_2 concentration of from 0.5 to 50 % by weight, more preferably from 1 to 30 % by weight. The aqueous stannic oxide sol may be prepared in any known method including, for example, an ion-exchanging method, a deflocculation method, a hydrolysis method, a reaction method, etc.

[0013] Examples of the ion-exchanging method include a method of processing a stannate such as sodium stannate or the like with a hydrogen-type cation exchange resin, a method of processing a stannic salt such as stannic chloride, stannic nitrate or the like with a hydroxyl-type anion exchange resin, etc. Examples of the deflocculation method include a method comprising washing a stannic hydroxide gel as prepared by neutralizing a stannic salt with a base or by neutralizing stannic acid with hydrochloric acid, followed by deflocculating the washed gel with an acid or a base, etc. Examples of the hydrolysis method include a method of hydrolyzing a tin alkoxide, a method comprising hydrolyzing a basic salt of stannic chloride under heat followed by removing the unnecessary acid from the resulting hydrolyzate, etc. Examples of the reaction method include a method of reacting metal tin powder with an acid.

[0014] The medium for the stannic oxide sol may be any of water, hydrophilic organic solvents and their mixtures, but is preferably water to give an aqueous sol. In general, the pH of the sol preferably falls between 0.2 and 11, in view of the stability of the sol. Within the range not interfering with the object of the invention, the stannic oxide sol may contain any optional components including, for example, an alkaline substance, an acidic substance, a hydroxycarboxylic acid and the like for stabilizing the sol.

[0015] On the other hand, the aqueous solution or suspension of an oxyzirconium salt preferably has an oxyzirconium salt concentration of from 0.5 to 50 % by weight, more preferably from 1 to 30 % by weight. The oxyzirconium salt includes, for example, zirconium oxychloride, zirconium oxynitrate, zirconium oxysulfate, oxyzirconium salts of organic acids such as zirconium oxyacetate, and also zirconium oxycarbonate, etc. Preferably, the oxyzirconium salts are used in the form of their aqueous solutions. However, when the aqueous stannic oxide sol to be mixed with them is acidic, even water-insoluble oxyzirconium salts such as zirconium oxycarbonate can be used herein in the form of their aqueous suspensions.

[0016] In the step (a), the aqueous stannic oxide sol is mixed with the aqueous solution or suspension of an oxyzirconium salt in a ratio by weight, ZrO_2/SnO_2 falling between 0.02 and 1.0. In particular, the stannic oxide sol in this is preferably an alkaline sol stabilized with an organic base such as an amine or the like. Mixing the stannic oxide sol with the aqueous solution or suspension of an oxyzirconium salt may be effected at a temperature generally falling between 0 and 100°C, but preferably between room temperature and 60°C. To mix them, the aqueous solution or suspension of an oxyzirconium salt may be added to the stannic oxide sol with stirring; or the stannic oxide sol may be added to the aqueous solution or suspension of an oxyzirconium salt. Preferred is the latter. Mixing them must be effected sufficiently, and is preferably continued for 0.5 to 3 hours or so.

<u>Step (b)</u>:

[0017] In step (b), the mixture obtained in the previous step (a) is heated to form an aqueous, stannic oxide-zirconium oxide composite sol having a particle size of from 4 to 50 nm. Preferably, the heat treatment is effected at a temperature falling between 60 and 200°C for 0.1 to 50 hours or so.

<u>Step (c)</u>:

[0018] Step (c) is to form a tungsten oxide-stannic oxide-silicon dioxide composite sol.

[0019] First prepared is an aqueous solution containing a tungstate, a stannate and a silicate in a ratio by weight, WO_3/SnO_2 and a ratio by weight, SiO_2/SnO_2 each falling generally between 0.1 and 100. In this stage, any of water, hydrophilic organic solvents or their mixtures may be used as the medium.

[0020] Salts of those tungstate, stannate and silicate include, for example, alkali metal salts, ammonium salts, amine salts, etc. Examples of the alkali metal salts include lithium salts, sodium salts, potassium salts, rubidium salts,

cesium salts. Preferred examples of the amine salts include salts with alkylamines such as ethylamine, triethylamine, isopropylamine, n-propylamine, isobutylamine, diisobutylamine, di(2-ethylhexyl)amine, etc.; salts with aralkylamines such as benzylamine, etc.; salts with alicyclic amines such as piperidine, etc.; salts with alkanolamines such as monoethanolamine, triethanolamine, etc. Especially preferred are sodium tungstate ($Na_2WO_4 \cdot 2H_2O$), sodium stannate ($Na_2SnO_3 \cdot 3H_2O$), and sodium silicate (water glass). Also usable herein are solutions prepared by dissolving tungsten oxide, tungstic acid, stannic acid, silicic acid or the like in an aqueous solution of an alkali metal hydroxide. As silicates, also usable are amine silicates and quaternary ammonium silicates prepared by adding an alkylamine such as ethylamine, triethylamine, isopropylamine, n-propylamine, isobutylamine, diisobutylamine, di(2-ethylhexyl)amine or the like to an activated silicic acid.

[0021] The method of preparing the aqueous solution containing a tungstate, a stannate and a silicate is not specifically defined. For example, employable is any of a method of dissolving powders of a tungstate, a stannate and a silicate in an aqueous medium to prepare an aqueous solution of the salts, a method of mixing an aqueous solution of a tungstate, an aqueous solution of a stannate and an aqueous solution of a silicate to prepare an aqueous solution of the salts, a method of adding powders of a tungstate and a stannate and an aqueous solution of a silicate to an aqueous medium to prepare an aqueous solution of the salts, etc.

[0022] In the method of mixing them, the aqueous tungstate solution preferably has a concentration of from 0.1 to 15 % by weight in terms of WO_3, and the aqueous stannate solution and the aqueous silicate solution each preferably have a concentration of from 0.1 to 30 % by weight in terms of SnO_2 and SiO_2, respectively.

[0023] In the step (c), preparing the aqueous solution containing a tungstate, a stannate and a silicate is preferably effected with stirring at a temperature falling between room temperature and 100°C or so, more preferably between room temperature and 60°C or so.

[0024] Next, the cations existing in the thus-prepared aqueous solution containing the salts are removed. To remove the cations, for example, employable is a method of contacting the solution with a hydrogen-type ion exchanger, or a method of subjecting the solution to salting-out treatment or the like. The hydrogen-type ion exchanger is not specifically defined, and may be any ordinary one, including, for example, commercially-available hydrogen-type cation exchange resins.

[0025] In that manner, obtained is an aqueous sol that contains tungsten oxide-stannic oxide-silicon dioxide composite colloid particles having a particle size of from 2 to 7 nm, preferably from 2 to 5 nm. The particle size of the colloid particles can be determined through electronic microscopy.

[0026] The total concentration of WO_3, SnO_2 and SiO_2 in the aqueous sol is generally at most 40 % by weight. If the concentration is higher than 40 % by weight, the stability of the sol will be poor. If too low, however, the sol will be impracticable. Therefore, the concentration is preferably at least 2 % by weight. More preferably, it falls between 5 and 30 % by weight. If the concentration of the aqueous sol, from which the cations have been removed, is low, it may be increased by any ordinary methods of concentrating the sol, for example, through evaporation, ultrafiltration or the like. Especially preferred is ultrafiltration. While being concentrated, the sol is preferably kept at a temperature not higher than 100°C or so, more preferably not higher than 60°C or so.

[0027] Where the sol is concentrated through ultrafiltration, the polyanions, ultra-fine particles and others existing in the sol will pass through the ultrafiltration membrane along with water. Therefore, the polyanions, ultra-fine particles and others which often unstabilize the sol can be removed from the sol.

[0028] In the aqueous sol, preferably, the tungsten oxide-stannic oxide-silicon dioxide composite colloid particles have a ratio by weight, WO_3/SnO_2 and a ratio by weight, SiO_2/SnO_2 each falling between 0.1 and 100. If the weight ratios overstep the defined range, the stability of the sol will be low, and, in addition, a modified composite sol having desired properties is difficult to obtain. Therefore, the weight ratios overstepping the defined ratio are unfavorable.

[0029] Preferably, the pH of the aqueous sol falls between 1 and 9. If its pH is lower than 1, the sol will be unstable; and if higher than 9, the tungsten oxide-stannic oxide-silicon dioxide composite colloid particles will easily dissolve in the liquid.

[0030] The pH control may be effected by the use of an acidic substance or an alkaline substance. The acidic substance is not specifically defined. Where an organosol to be mentioned below is prepared, preferred is a hydroxycarboxylic acid in view of the stability of the sol. Examples of the hydroxycarboxylic acid include lactic acid, tartaric acid, citric acid, gluconic acid, malic acid, glycollic acid, etc. One or more hydroxycarboxylic acids may be used either singly or as combined. The amount of the acid to be used is preferably smaller than 30 % by weight of the total amount of WO_3, SnO_2 and SiO_2 in the sol. Too much acid over 30 % by weight, if used, will lower the waterproofness of the cured film of the modified composite sol from the sol.

[0031] Examples of the alkaline substance include alkali metal hydroxides with Li, Na, L, Rb, Cs or the like; ammonia; alkylamines such as ethylamine, triethylamine, isopropylamine, n-propylamine, etc.; aralkylamines such as benzylamine, etc.; alicyclic amines such as piperidine, etc.; alkanolamines such as monoethanolamine, triethanolamine, etc. One or more alkaline substances may be used either singly or as combined, or may be combined with above-mentioned acidic substances.

[0032] The thus-obtained, tungsten oxide-stannic oxide-silicon dioxide composite sol is a colorless transparent, or colloidally-tinted liquid. The sol is stable for 3 months or longer at room temperature, and for 1 month or longer even at 60°C, without forming any precipitate therein, or without being thickened or gelled.

[0033] Water in the aqueous sol prepared in the step (c) may be substituted with a hydrophilic organic solvent to give a hydrophilic organic solvent sol, which is referred to as an organosol.

[0034] The tungsten oxide-stannic oxide-silicon dioxide composite sol obtained in the step (c) contains composite particles of tungsten oxide-stannic oxide-silicon dioxide with stannic oxide, tungsten oxide and silicon dioxide being compounded (in solid solution) uniformly on the atomic level. Therefore, the sol differs from a mixed sol as prepared by merely mixing three sols, tungsten oxide sol, stannic oxide sol and silicon dioxide sol. In the composite sol of tungsten oxide-stannic oxide-silicon dioxide, the composite particles of tungsten oxide-stannic oxide-silicon dioxide form a solid solution. Therefore, even when subjected to solvent substitution, the composite sol is not decomposed into the individual tungsten oxide particles, stannic oxide particles and silicon dioxide particles. In addition, the film of the composite sol of tungsten oxide-stannic oxide-silicon dioxide formed on a substrate has better waterproofness, better moisture resistance and better weather resistance, as compared with that of a composite sol of tungsten oxide-stannic oxide formed on the same.

Step (d):

[0035] Step (d) is to mix the aqueous, stannic oxide-zirconium oxide composite sol prepared in the previous step (b) with the tungsten oxide-stannic oxide-silicon dioxide composite sol prepared in the step (c) to form an aqueous, modified stannic oxide-zirconium oxide composite sol.

[0036] In this step, the stannic oxide-zirconium oxide composite sol (nuclei sol) prepared in the previous step (b) is mixed with the tungsten oxide-stannic oxide-silicon dioxide composite sol (cover sol) prepared in the step (c), in such a ratio that the total of WO_3, SnO_2 and SiO_2 in the latter sol is from 2 to 100 parts by weight relative to 100 parts by weight of the total of the metal oxides (ZrO_2 + SnO_2) in the former sol. Advantageously, the sols are mixed while being strongly stirred at a temperature falling generally between 0 and 100°C, but preferably between room temperature and 60°C.

[0037] If the total amount of the metal oxides (WO_3 + SnO_2 + SiO_2) in the cover sol is smaller than 2 parts by weight relative to 100 parts by weight of the total amount of the metal oxides (ZrO_2 + SnO_2) in the nuclei sol, a stable composite sol could not be obtained; but if larger than 100 parts by weight, a mixed sol of a modified stannic oxide-zirconium oxide composite sol and the remaining nuclei sol will be formed. Therefore, overstepping the defined range for the blend ratio is unfavorable.

[0038] In the manner as above, the colloid particles of the tungsten oxide-stannic oxide-silicon dioxide composite sol are bonded to the surfaces of the colloid particles of the stannic oxide-zirconium oxide composite sol, whereby the surfaces of the stannic oxide-zirconium oxide composite colloid particles are coated with the tungsten oxide-stannic oxide-silicon dioxide composite colloid particles to give modified stannic oxide-zirconium oxide composite colloid particles in which the stannic oxide-zirconium oxide composite colloid particles serve as the nuclei and which exhibit the properties of the tungsten oxide-stannic oxide-silicon dioxide composite that covers the nuclei. In this step, the modified stannic oxide-zirconium oxide composite colloid particles are formed in the form of a sol where the particles are stably dispersed in a liquid medium.

[0039] The modified stannic oxide-zirconium oxide composite colloid particles in the sol thus obtained through the mixing operation in the step (d) can be observed with an electronic microscope, and they generally have a particle size of from 4.5 to 60 nm. The sol obtained through the mixing operation has a pH of approximately from 1 to 9. However, it contains many anions of Cl^-, NO_3^-, CH_3COO^- and others that are derived from the oxyzirconium salt used for the modification. Therefore, the colloid particles in the sol are micro-aggregated, and the transparency of the sol is low.

[0040] The modified stannic oxide-zirconium oxide composite colloid particles that are covered with the tungsten oxide-stannic oxide-silicon dioxide composite colloid particles in the invention are charged in minus in the sol containing them. On the other hand, the stannic oxide-zirconium oxide composite colloid particles are charged in plus, while the tungsten oxide-stannic oxide-silicon dioxide composite colloid particles are charged in minus. Therefore, it is believed that, in the mixing operation in the step (d), the plus-charged stannic oxide-zirconium oxide composite colloid particles will electrically attract the minus-charged tungsten oxide-stannic oxide-silicon dioxide composite colloid particles around them, whereby the thus-attracted tungsten oxide-stannic oxide-silicon dioxide composite colloid particles will chemically bond onto the surfaces of the plus-charged stannic oxide-zirconium oxide composite colloid particles, and, as a result, the surfaces of the plus-charged particles that serve as the nuclei will be covered with the tungsten oxide-stannic oxide-silicon dioxide composite to give the modified stannic oxide-zirconium oxide composite colloid particles.

Step (e):

[0041] Step (e) is to contact the aqueous, modified stannic oxide-zirconium oxide composite sol prepared in the

previous step (d) with an anion exchanger to thereby remove the anions from the sol.

[0042] Contacting the sol with an anion exchanger may be effected at a temperature generally not higher than 100°C, but preferably at a temperature falling between room temperature and 60°C. As the anion exchanger, employable are any commercially-available hydroxyl-type anion exchange resins, but preferred are strong base-type anion exchange resins such as Amberlite 410. Advantageously, in this step, the sol prepared in the step (d) is treated with such an anion exchanger while the metal oxide concentration in the sol is controlled to fall between 1 and 10 % by weight.

[0043] The anions are removed from the sol in the manner as above, and a stable sol of modified stannic oxide-zirconium oxide composite colloid particles having a pH of from 3 to 11 and having high transparency is obtained.

[0044] Where the concentration of the modified stannic oxide-zirconium oxide composite sol thus obtained is desired to be increased more, the sol may be concentrated to have a concentration of up to at most about 50 % by weight, in an ordinary manner, for example, through evaporation, ultrafiltration or the like. Where the pH of the sol is desired to be changed, the above-mentioned alkali metal hydroxide, ammonia, amine, hydroxycarboxylic acid or the like may be added to the concentrated sol. In particular, the sol having a total concentration of the metal oxides (ZrO_2 + SnO_2) and (WO_3 + SnO_2 + SiO_2) of from 10 to 40 % by weight is preferred for practical use.

[0045] If the pH of the modified stannic oxide-zirconium oxide composite sol is lower than 3, the sol will be unstable; but if higher than 11, the tungsten oxide-stannic oxide-silicon dioxide composite that covers the modified stannic oxide-zirconium oxide composite colloid particles will easily dissolve in the liquid. If the total concentration of the metal oxides (ZrO_2 + SnO_2) and (WO_3 + SnO_2 + SiO_2) in the sol of the modified stannic oxide-zirconium oxide composite colloid particles is higher than 50 % by weight, the sol will be unstable.

[0046] Where the modified stannic oxide-zirconium oxide composite sol is an aqueous sol, the aqueous medium in the aqueous sol may be substituted with a hydrophilic organic solvent whereby the aqueous sol may be converted into an organosol. The substitution may be effected by any ordinary method of, for example, evaporation, ultrafiltration or the like. Examples of the hydrophilic organic solvent include lower alcohols such as methyl alcohol, ethyl alcohol, isopropyl alcohol, etc.; linear amides such as dimethylformamide, N,N-dimethylacetamide, etc.; cyclic amides such as N-methyl-2-pyrrolidone, etc.; glycols such as ethyl cellosolve, ethylene glycol, etc.

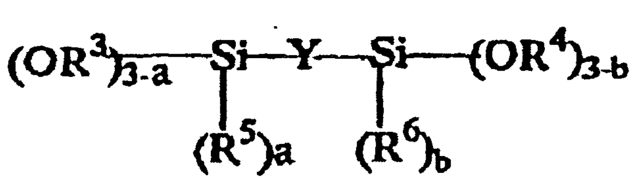
[0047] The sol prepared through the above-mentioned steps (a) to (e) and containing the modified stannic oxide-zirconium oxide composite colloid particles to be the component (A) in the coating agent for use in the invention is stable for 3 months or longer at room temperature and for 1 month or longer even at 60°C, without forming any precipitate therein, or without being thickened or gelled. The sol is colorless and transparent, and its cured film has a refractive index of approximately from 1.7 to 1.8, and has high bonding strength, high hardness, good lightproofness, good electrification resistance, good heat resistance and good abrasion resistance. In particular, the waterproofness and the moisture resistance of the cured film are much higher than those of conventional films. The reason will be because the silicon dioxide component in the tungsten oxide-stannic oxide-silicon oxide colloid particles will form siloxane bonding in the cured film, thereby improving the waterproofness and the moisture resistance of the film.

[0048] The coating agent for use in the invention contains an organosilicon compound as the component (B). The organosilicon compound is, for example, at least one selected from compounds of a general formula (I):

$$R^1_nSi(OR^2)_{4-n} \qquad (I)$$

wherein R^1 represents a monovalent hydrocarbon group having from 1 to 20 carbon atoms, and having or not having a functional group; R^2 represents an alkyl, aryl, aralkyl or acyl group having from 1 to 8 carbon atoms; n represents 0, 1 or 2; and plural R^1's, if any, may be the same or different, and plural R^2O's may be the same or different,

compounds of a general formula (II):



(II)

wherein R^3 and R^4 each represent an alkyl or acyl group having from 1 to 4 carbon atoms, and may be the same

or different; R^5 and R^6 each represent a monovalent hydrocarbon group having from 1 to 5 carbon atoms, and having or not having a functional group, and may be the same or different; Y represents a divalent hydrocarbon group having from 2 to 20 carbon atoms; a and b each represent 0 or 1; and plural OR^3's may be the same or different, and plural OR^4's may be the same or different,

and their hydrolyzates.

[0049] In formula (I), the monovalent hydrocarbon group having from 1 to 20 carbon atoms for R^1 includes a linear, branched or cyclic alkyl group having from 1 to 20 carbon atoms, a linear, branched or cyclic alkenyl group having from 2 to 20 carbon atoms, an aryl group having from 6 to 20 carbon atoms, and an aralkyl group having from 7 to 20 carbon atoms. The alkyl group having from 1 to 20 carbon atoms is preferably one having from 1 to 10 carbon atoms, including, for example, a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, a pentyl group, a hexyl group, an octyl group, a cyclopentyl group, a cyclohexyl group, etc. The alkenyl group having from 2 to 20 carbon atoms is preferably an alkenyl group having from 2 to 10 carbon atoms, including, for example, a vinyl group, an allyl group, a butenyl group, a hexenyl group, an octenyl group, etc. The aryl group having from 6 to 20 carbon atoms is preferably one having from 6 to 10 carbon atoms, including, for example, a phenyl group, a tolyl group, a xylyl group, a naphthyl group, etc. The aralkyl group having from 7 to 20 carbon atoms is preferably one having from 7 to 10 carbon atoms, including, for example, a benzyl group, a phenethyl group, a phenylpropyl group, a naphthylmethyl group, etc.

[0050] These hydrocarbon groups may have a functional group introduced thereinto. The functional group includes, for example, a halogen atom, a glycidoxy group, an epoxy group, an amino group, a mercapto group, a cyano group, a (meth)acryloyloxy group, etc. As the hydrocarbon group having such a functional group, preferred is an alkyl group having from 1 to 10 carbon atoms and having a functional group. This includes, for example, a γ-chloropropyl group, a 3,3,3-trichloropropyl group, a chloromethyl group, a glycidoxymethyl group, an α-glycidoxyethyl group, a β-glycidoxyethyl group, an α-glycidoxypropyl group, a β-glycidoxypropyl group, a γ-glycidoxypropyl group, an α-glycidoxybutyl group, a β-glycidoxybutyl group, a γ-glycidoxybutyl group, a δ-glycidoxybutyl group, a (3,4-epoxycyclohexyl)methyl group, a β-(3,4-epoxycyclohexyl)ethyl group, a γ-(3,4-epoxycyclohexyl)propyl group, a δ-(3,4-epoxycyclohexyl)butyl group, an N-(β-aminoethyl)-γ-aminopropyl group, a γ-aminopropyl group, a γ-mercaptopropyl group, a β-cyanoethyl group, a γ-methacryloyloxypropyl group, a γ-acryloyloxypropyl group, etc.

[0051] On the other hand, the alkyl group having from 1 to 8 carbon atoms for R^2 may be linear, branched or cyclic, including, for example, a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, a pentyl group, a hexyl group, a cyclopentyl group, a cyclohexyl group, etc. The aryl group includes, for example, a phenyl group, a tolyl group, etc. The aralkyl group includes, for example, a benzyl group, a phenethyl group, etc. The acyl group includes, for example, an acetyl group, etc.

[0052] n is 0, 1 or 2; and plural R^1,s, if any, may be the same or different, and plural R^2O's may be the same or different.

[0053] Examples of the compounds of formula (I) include methyl silicate, ethyl silicate, n-propyl silicate, isopropyl silicate, n-butyl silicate, sec-butyl silicate, tert-butyl silicate, tetraacetoxysilane, methyltrimethoxysilane, methyltripropoxysilane, methyltriacetoxysilane, methyltributoxysilane, methyltripropoxysilane, methyltriamyloxysilane, methyltriphenoxysilane, methyltribenzyloxysilane, methyltriphenethyloxysilane, glycidoxymethyltrimethoxysilane, glycidoxymethyltriethoxysilane, a-glycidoxyethyltrimethoxysilane, α-glycidoxyethyltriethoxysilane, β-glycidoxyethyltriethoxysilane, α-glycidoxypropyltrimethoxyslane, α-glycidoxypropyltriethoxysilane, β-glycidoxypropyltrimethoxysilane, β-glycidoxypropyltriethoxysilane, γ-glycidoxypropyltrimethoxysilane, γ-glycidoxypropyltriethoxysilane, γ-glycidoxypropyltripropoxysilane, γ-glycidoxypropyltriphenoxysilane, α-glycidoxybutyltrimethoxysilane, α-glycidoxybutyltriethoxysilane, β-glycidoxybutyltrimethoxysilane, γ-glycidoxybutyltriethoxysialne, γ-glycidoxybutyltrimethoxysilane, γ-glycidoxybutyltriethoxysilane, δ-glycidoxybutyltrimethoxysilane, δ-glycidoxybutyltriethoxysilane, (3,4-epoxycyclohexyl)methyltrimethoxysilane, (3,4-epoxycyclohexyl)methyltriethoxysilane, β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, β-(3,4-epoxycyclohexyl)ethyltriethoxysilane, β-(3,4-epoxycyclohexyl)ethyltripropoxysilane, β-(3,4-epoxycyclohexyl)ethyl)tributoxysilane, β-(3,4-epoxycyclohexyl)ethyltriphenoxysilane, γ-(3,4-epoxycyclohexyl)propyltrimethoxysilane, γ-(3,4-epoxycyclohexyl)propyltriethoxysilane, δ-(3,4-epoxycyclohexyl)butyltrimethoxysilane, δ-(3,4-epoxycyclohexyl)butyltriethoxysilane, glycidoxymethylmethyldimethoxysilane, glycidoxymethylmethyldiethoxysilane, α-glycidoxyethylmethyldimethoxysilane, α-glycidoxyethylmethyldiethoxysilane, β-glycidoxyethylmethyldimethoxysilane, β-glycidoxyethylmethyldiethoxysilane, α-glycidoxypropylmethyldimethoxysilane, α-glycidoxypropylmethyldiethoxysilane, β-glycidoxypropylmethyldimethoxysilane, α-glycidoxypropylmethyldiethoxysilane, γ-glycidoxypropylmethyldimethoxysilane, γ-glycidoxypropylmethyldiethoxysilane, γ-glycidoxypropylmethyldipropoxysilane, γ-glycidoxypropyltrimethoxysilane, γ-glycidoxypropylmethyldiphenoxysilane, γ-glycidoxypropylethyldimethoxysilane, γ-glycidoxypropylethyldiethoxysilane, γ-glycidoxypropylvinyldimethoxysilane, γ-glycidoxypropylvinyldiethoxysilane, γ-glycidoxypropylphenyldimethoxysilane, γ-glycidoxypropylphenyldiethoxysilane, ethyltrimethoxysilane, ethyltriethoxysilane, vinyltrimethoxysilane, vinyltriacetoxysilane, vinyltriethoxysilane, phenyltrimethoxysilane, phenyltriethoxysilane,

phenyltriacetoxysilane, γ-chloropropyltrimethoxysilane, γ-chloropropyltriacetoxysilane, 3,3,3-trifluoropropyltrimethoxysilane, γ-methacryloyloxypropyltrimethoxysilane, γ-mercaptopropyltrimethoxysilane, γ-mercaptopropyltriethoxysilane, β-cyanoethyltriethoxysilane, chloromethyltrimethoxysilane, chloromethyltriethoxysilane, N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane, N-(β-aminoethyl)-γ-aminopropylmethyldimethoxysilane, γ-aminopropylmethyldimethoxysilane, N-(β-aminoethyl)-γ-aminopropylmethyldimethoxysilane, N-(β-aminoethyl)-γ-aminopropylmethyldiethoxysilane, dimethyldimethoxysilane, phenylmethyldimethoxysilane, dimethyldiethoxysilane, phenylmethyldiethoxysilane, γ-chloropropylmethyldimethoxysilane, γ-chloropropylmethyldiethoxysilane, dimethyldiacetoxysilane, γ-methacryloyloxypropylmethyldimethoxysilane, γ-methacryloyloxypropylmethyldiethoxysilane, γ-mercaptopropylmethyldimethoxysilane, γ-mercaptopropylmethyldiethoxysilane, methylvinyldimethoxysilane, methylvinyldiethoxysilane, etc.

[0054] On the other hand, in formula (II), the alkyl group having from 1 to 4 carbon atoms for R^3 and R^4 includes, for example, a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, etc. The acyl group is preferably an acetyl group. R^3 and R^4 may be the same or different. The monovalent hydrocarbon group having from 1 to 5 for R^5 and R^6 includes, for example, an alkyl group having from 1 to 5 carbon atoms, and an alkenyl group having from 2 to 5 carbon atoms. These may be linear or branched. Examples of the alkyl group include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, a sec-butyl group, a tert-butyl group, a pentyl group, etc. The alkenyl group includes, for example, a vinyl group, an allyl group, a butenyl group, etc.

[0055] These hydrocarbon groups may have a functional group introduced thereinto. As examples of the functional group and the functional group-having hydrocarbon group, referred to are those mentioned hereinabove for R^1 in formula (I). R^5 and R^6 may be the same or different. The divalent hydrocarbon group having from 2 to 20 carbon atoms for Y is preferably an alkylene or alkylidene group having from 2 to 10 carbon atoms, including, for example, a methylene group, an ethylene group, a propylene group, a butylene group, an ethylidene group, a propylidene group, etc.

[0056] a and b each represent 0 or 1. Plural OR^3's may be the same or different, and plural OR^4's may be the same or different.

[0057] Examples of the compounds of formula (II) include methylenebis (methyldimethoxysilane), ethylenebis(ethyldimethoxysilane), propylenebis(ethyldiethoxysilane), butylenebis(methyldiethoxysilane), etc.

[0058] One or more suitably selected from the compounds of formulae (I) and (II) and their hydrolyzates may be used either singly or as combined, as the organosilicon compound for the component (B) to be in the coating agent for use in the invention. The hydrolyzates may be prepared by adding an aqueous basic solution such as an aqueous solution of sodium hydroxide, ammonia or the like, or an aqueous acidic solution such as an aqueous solution of acetic acid, an aqueous solution of citric acid or the like, to the organosilicon compound of formulae (I) and (II), followed by stirring the resulting mixture.

[0059] Regarding the ratio of the component (A), modified stannic oxide-zirconium oxide composite colloid particles to the component (B), organosilicon compound in the coating agent for use in the invention, it is desirable that the coating agent contains from 1 to 500 parts by weight, in terms of its solid content, of the component (A) relative to 100 parts by weight of the component (B). If the amount of the component (A) is smaller than 1 part by weight, the refractive index of the cured film to be formed of the coating agent will be small. If so, the applications of the coating agent to substrates will be limited. If, on the other hand, it is larger than 500 parts by weight, the interface between the cured film and the substrate will be cracked, and, in addition, the transparency of the cured film will be low.

[0060] The optical substrate to be used in the optical element of the invention includes plastic substrates of, for example, methyl methacrylate homopolymers, copolymers from monomer components of methyl methacrylate and one or more comonomers, diethylene glycol bisallylcarbonate homopolymers, copolymers from monomer components of diethylene glycol bisallylcarbonate and one or more comonomers, sulfur-containing copolymers, halogen-containing copolymers, polycarbonates, polystyrenes, polyvinyl chlorides, unsaturated polyesters, polyethylene terephthalates, polyurethanes, polythiourethanes, etc. Plastic lenses having a refractive index of from 1.55 to 1.62 are suitable as the substrate, in consideration of the esthetic appearances of the coated lenses (this means that the coated lenses do not form interference fringes to be caused by the difference in the refractive index between the coating film and the lens substrate).

[0061] The coating agent for use in the invention may optionally contain a curing agent for promoting the reaction, fine metal oxide particles for controlling the refractive index of the cured film so as to make the film compatible with various substrates, and various organic solvents and surfactants for improving the wettability of the coating agent applied to substrates and for improving the smoothness of the cured film. In addition, UV absorbents, antioxidants, light stabilizers and others may also be added to the coating agent, so far as they do not have any negative influences on the physical properties of the cured film.

[0062] Examples of the curing agent include amines such as allylamine, ethylamine, etc.; various acids and bases including Lewis acids and Lewis bases, salts or metal salts with organic carboxylic acids, chromic acid, hypochlorous acid, boric acid, perchloric acid, bromic acid, selenious acid, thiosulfuric acid, orthosilicic acid, thiocyanic acid, nitrous acid, aluminic acid, carbonic acid or the like; as well as metal alkoxides with aluminium, zirconium, titanium or the like,

and their metal chelate compounds. A typical curing agent is aluminium perchlorate.

[0063] The fine metal oxide particles may be any conventional ones, including, for example, fine particles of aluminium oxide, titanium oxide, antimony oxide, zirconium oxide, silicon oxide, cerium oxide, iron oxide, etc.

[0064] To cure it, in general, the coating agent is dried with hot air or is exposed to active energy radiations. Regarding the curing conditions, the coating agent is preferably exposed to hot air at 70 to 200°C, more preferably at 90 to 150°C. The active energy radiations include IR rays, etc. As not generating heat, such radiations cause little damage to the coating agent exposed thereto.

[0065] For forming a cured film of the coating agent on a substrate in the invention, employed is the above-mentioned method of applying the coating agent to a substrate. Applying it a substrate may be effected in any ordinary manner, for example, through dipping, spin-coating, spraying, etc. In view of the plane accuracy, especially preferred is a dipping method and a spin-coating method.

[0066] Prior to being coated with the coating agent, the substrate may be subjected to chemical treatment with any of acids, alkalis and various organic solvents, or to physical treatment with plasma, UV rays and the like, or to detergent treatment with various detergents, or to sand-blasting treatment, or to primer treatment with various resins, whereby the adhesiveness of the substrate and the cured film formed thereon could be increased.

[0067] If desired, an antireflection film of an inorganic oxide deposit may be provided on the cured film having been formed on the optical element of the invention in the manner mentioned above. The antireflection film is not specifically defined, and may be any conventional, single-layered or multi-layered antireflection film of an inorganic oxide deposit. Some examples of the antireflection film are described in, for example, Japanese Patent Laid-Open Nos. 262104/1990 and 116003/1981, any of which are employable herein.

[0068] The cured film of the coating agent of the invention can be a high-refractive-index film serving as a reflective film. In addition, the cured film may be further processed to make it have additional functions of antifogging properties, photochromic properties, stain-resistant properties and others, and the thus-processed films could be used as a multi-functional films.

[0069] The cured film-coated optical element of the invention can be used not only for lenses for glasses but also for lenses for cameras, windshields for cars, optical filters to be mounted on displays for word processors, etc.

[Examples]

[0070] Now, the invention is described in more detail with reference to the following Examples, which, however, are not intended to restrict the scope of the invention.

[0071] The physical properties of the cured film-coated optical elements produced in Examples were measured according to the methods mentioned below.

(1) Test for Initial Physical Properties:

[0072] The cured film-coated optical elements produced were left at room temperature for 1 day, and evaluated for the following (i) to (iv):

(i) Evaluation of Scratch Resistance:

[0073] The surface of the cured film was rubbed with steel wool #0000 20 times back and force, with a load of 2 kg being applied thereto, and macroscopically checked for its scratch resistance. The samples thus tested were judged according to the following criteria:

OO: Samples scratched little.
O: Samples with less than 5 scratches.
Δ: Samples with from 5 to less than 10 scratches.
X: Samples with 10 or more scratches, including those scratched to the same level as non-coated optical substrates.

(ii) Evaluation of Interference Fringes:

[0074] The cured film-coated optical elements were macroscopically checked by the light from a fluorescent lamp. These were judged according to the following criteria:

OO: No interference fringe seen.
O: Few interference fringe seen.

Δ: A few interference fringes seen.
X: Many interference fringes seen.

(iii) Evaluation of Adhesiveness:

[0075] The cured film was cut to have 100 cross-cuts of 1.5 mm × 1.5 mm each. An adhesive tape (trade name, Sellotape from Nichiban) was firmly stuck on its cross-cut area, and rapidly peeled off, and the cured film was checked as to whether or not its cross-cuts peeled along with the adhesive tape. The samples were judged according to the following criteria:

OO: Not peeled.
O: 1 to 10 cross-cuts peeled.
Δ: 11 to 50 cross-cuts peeled.
X: 51 to 100 cross-cuts peeled.

(iv) Evaluation of Transparency:

[0076] The cured film was macroscopically checked for its transparency by the use of the light from a fluorescent lamp in a dark room. The samples were judged according to the following criteria:

OO: Not cloudy.
O: Cloudy little.
Δ: Cloudy a little.
X: Much cloudy.

(2) Test for Moisture Resistance:

[0077] The optical elements were left in a thermo-hygrostat tester (from Yamato Engineering) at 40°C and 90 % RH for 1 week, and then subjected to the tests (i) to (iv).

(3) Test for Lightproofness:

[0078] The optical elements were exposed to a xenon long-life weather meter (from Suga Test Machine) for 200 hours, and then subjected to the tests (i) to (iv).

Production Example 1

Production of modified stannic oxide-zirconium oxide composite sol

⟨Preparation of stannic oxide sol⟩

[0079] 1200 g of an aqueous, pale yellow, transparent stannic oxide sol (this was obtained through reaction of metal tin powder, an aqueous solution of hydrochloric acid and an aqueous solution of hydrogen peroxide, and had a specific gravity of 1.420; a pH of 0.40; a viscosity just after stirring of 32 mPa • s; an SnO_2 content of 33.0 % by weight; an HCl content of 2.56 % by weight; a spindle-like colloid particle diameter measured with an electronic microscope of at most 10 nm; a specific surface area of the particles as measured according to the BET method of 120 m^2/g; a particle diameter as calculated from the specific surface area of 7.2 nm; and a particle diameter as measured according to the kinematic light-scattering method by the use of a US Coulter's N_4 device of 107 nm) were dispersed in 10800 g of water, to which was added 4.8 g of isopropylamine. Next, the resulting liquid was passed through a column filled with a hydroxyl-type anion exchange resin to obtain 13440 g of an aqueous, alkaline stannic oxide sol. The sol was stable and had a colloid-like tint, but its transparency was extremely high. It had a specific gravity of 1.029, a pH of 9.80, a viscosity of 1.4 mPa • s, an SnO_2 content of 2.95 % by weight, and an isopropylamine content of 0.036 % by weight.

Step (a):

[0080] 10791 g (409.5 g in terms of SnO_2) of the aqueous, alkaline stannic oxide sol was added to 3043 g (60.87 g in terms of ZrO_2) of an aqueous solution of zirconium oxychloride (having a ZrO_2 concentration of 2.0 % by weight; this was prepared by dissolving a chemical reagent zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) in water), with stirring at

room temperature, and further stirred for 2 hours. The resulting mixture was a colloidally-tinted, highly-transparent sol having a ratio by weight, ZrO_2/SnO_2 of 0.15 and a pH of 1.50.

Step (b) (preparation of stannic oxide-zirconium oxide composite):

[0081] The mixture prepared in the step (a) was heated at 90°C for 5 hours with stirring to obtain 13834 g of a stannic oxide-zirconium oxide composite sol. The sol had a colloid-like tint but was highly transparent, having an SnO_2 content of 2.96 % by weight, a ZrO_2 concentration of 0.44 % by weight, a total (SnO_2 + ZrO_2) content of 3.40 % by weight, a pH of 1.45, and a particle size of 9.0 nm.

Step (c) (preparation of tungsten oxide-stannic oxide-silicon dioxide composite sol):

[0082] 113 g of diatom (having an SiO_2 content of 29.0 % by weight) was dissolved in 2353.7 g of water, and 33.3 g of sodium tungstate $Na_2WO_4 \cdot 2H_2O$ (having a WO_3 content of 71 % by weight) and 42.45 g of sodium stannate $NaSnO_3 \cdot H_2O$ (having an SnO_2 content of 55 % by weight) were dissolved therein. Next, this was passed through a column filled with a hydrogen-type cation exchange resin to obtain 3150 g of an acidic tungsten oxide-stannic oxide-silicon dioxide composite sol (having a pH of 2.1, a WO_3 content of 0.75 % by weight, an SnO_2 content of 0.75 % by weight, an SiO_2 content of 1.00 % by weight, a ratio by weight, WO_3/SnO_2 of 1.0, a ratio by weight, SiO_2/SnO_2 of 1.33, and a particle size of 2.5 nm).

Step (d):

[0083] To 3150 g (78.83 g in terms of WO_3 + SnO_2 + SiO_2) of the tungsten oxide-stannic oxide-silicon dioxide composite sol prepared in the step (c), added was 11592.6 g (394.1 g in terms of ZrO_2 + SnO_2) of the stannic oxide-zirconium oxide composite sol prepared in the step (b), with stirring at room temperature over a period of 20 minutes, and further stirred for 30 minutes. The resulting mixture had a ratio by weight of the tungsten oxide-stannic oxide-silicon dioxide composite colloid (WO_3 + SnO_2 + SiO_2) to the stannic oxide-zirconium oxide composite colloid (ZrO_2 + SnO_2), (WO_3 + SnO_2 + SiO_2)/(ZrO_2 + SnO_2), of 0.20, a pH of 2.26, and a total metal oxide content of 3.2 % by weight, and was somewhat cloudy as containing micro-aggregates of the colloid particles.

Step (e) (Preparation of modified stannic oxide-zirconium oxide composite sol):

[0084] 9.5 g of diisobutylamine was added to 14742.6 g of the mixture prepared in the step (d), and the resulting mixture was passed through a column filled with a hydroxyl-type anion exchange resin (Amberlite 410) at room temperature, and thereafter aged under heat at 80°C for 1 hour to obtain 16288 g of an aqueous, modified stannic oxide-zirconium oxide composite sol (thin liquid). The sol had a colloid-like tint but was highly transparent, having a total metal oxide content 2.90 % by weight, and a pH of 10.43.

[0085] Using a filtration device, the aqueous, modified stannic oxide-zirconium oxide composite sol (thin liquid) prepared in the step (e) was concentrated at room temperature through an ultrafiltration membrane (this is for fractionation of fractions having a molecular weight of 50,000) to obtain 2182 g of an aqueous, high-concentration, modified stannic oxide-zirconium oxide composite sol. The sol was stable, having a pH of 8.71, and a total metal oxide (ZrO_2 + SnO_2 + WO_3 + SiO_2) content of 18.3 % by weight.

[0086] To 2182 g of the aqueous, high-concentration, modified stannic oxide-zirconium oxide composite sol, added were 4.0 g of tartaric acid, 6.0 g of diisobutylamine and one drop of a defoaming agent (SN Deformer 483 from Sun-Nopco), with stirring at room temperature, and further stirred for 1 hour. From the sol, water was removed through evaporation under normal pressure, in a reaction flask equipped with a stirrer, with 20 liters of methanol being added thereto little by little. In that manner, water in the aqueous sol was substituted with methanol, and 1171 g of a methanol sol of modified stannic oxide-zirconium oxide composite was obtained. The sol had a specific gravity of 1.124, a pH of 7.45 (in the form of a 1/1 sol/water, by weight, mixture), a viscosity of 2.3 mPa • s, a total metal oxide (ZrO_2 + SnO_2 + WO_3 + SiO_2) content of 32.7 % by weight, a water content of 0.47 % by weight, and a particle size as measured through electronic microscopy of from 10 to 15 nm.

[0087] The sol had a colloid-like tint and was highly transparent. Even after left at room temperature for 3 months, it was still stable with no change, that is, it did not form any precipitate, it did not become cloudy, and it did not thicken. The dried sol had a refractive index of 1.76.

Example 1:

(1) Preparation of Coating Agent:

[0088] 15 parts by weight of γ-glycidoxypropyltrimethoxysilane and 49 parts by weight of the methanol sol of modified stannic oxide-zirconium oxide composite prepared in Production Example 1 were put into a rector equipped with a rotor, and stirred at 4°C for 3 hours. Then, 3.5 parts by weight of 0.001 N hydrochloric acid was gradually dripped into the reactor, and stirred at 4°C for 48 hours.

[0089] Next, to this were added 30 parts by weight of propylene glycol monomethyl ether and 0.04 parts by weight of a silicone-type surfactant, and stirred at 4°C for 3 hours, and then 0.60 parts by weight of acetylacetonatoaluminium and 0.05 parts by weight of aluminium perchlorate (from Aldrich) were added thereto and mixed. After having been stirred at 4°C for 3 days, this was kept static at 4°C for 2 days to obtain a coating agent.

(2) Formation and Evaluation of Cured Film:

[0090] A plastic lens substrate (from HOYA; this is a plastic lens for glasses, having a refractive index of 1.60) that had been pre-treated in an aqueous solution of 10 wt.% NaOH was immersed in the coating agent prepared in above (1), for 5 seconds. After having been thus immersed, the plastic lens was pulled out at a pulling-out rate of 20 cm/min, and heated at 120°C for 1 hour, whereby a cured film was formed on it. The cured film-coated plastic lens was tested, and its data are given in Table 1.

Example 2:

[0091] The cured film-coated plastic lens substrate obtained in Example 1 was disposed in a vapor deposition device, and heated therein at 85°C while the device was degassed to a degree of 2×10^{-5} Torr. In that condition, the vaporizing materials also disposed in the device to form an antireflection film on the cured film of the lens substrate were vaporized and deposited on the cured film by heating them with electron beams thereby forming on the cured film an antireflection film. The antireflection film was composed of a subbing layer of SiO_2 having a thickness of 0.6 λ; a mixed layer (nd = 2.05, nλ = 0.075λ) of Ta_2O_5, ZrO_2 and Y_2O_3 formed on the subbing layer; a first refractive layer (nd = 1.46, nλ = 0.056λ) of SiO_2; a mixed layer (nd = 2.05, nλ = 0.075λ) of Ta_2O_5, ZrO_2 and Y_2O_3; and a second low-refractive-index layer (nd = 1.46, nλ = 0.25λ) of SiO_2, layered in that order. The thus-coated plastic lens was tested, and its data are given in Table 1.

Example 3:

[0092] A cured film-coated plastic lens was produced in the same manner as in Example 1, except that 15 parts by weight of β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane was used in place of 15 parts by weight of γ-glycidoxypropyltrimethoxysilane in the step of Example 1(1). Its data are given in Table 1.

Example 4:

[0093] The same process as in Example 2 was repeated, except that the cured film-coated plastic lens substrate produced in Example 3 was used in place of that produced in Example 1. The data of the coated lens are given in Table 1.

Example 5:

[0094] A cured film-coated plastic lens was produced in the same manner as in Example 1, except that 15 parts by weight of tetramethoxysilane (methyl silicate) was used in place of 15 parts by weight of γ-glycidoxypropyltrimethoxysilane, and, as the curing agent, 0.60 parts by weight of trimellitic anhydride was used in place of 0.60 parts by weight of acetylacetonatoaluminium in the step of Example 1(1). Its data are given in Table 1.

Example 6:

[0095] The same process as in Example 2 was repeated, except that the cured film-coated plastic lens substrate produced in Example 5 was used in place of that produced in Example 1. The data of the coated lens are given in Table 1.

Comparative Example 1:

[0096] A cured film-coated plastic lens was produced in the same manner as in Example 1, except that 49 parts by weight of a modified stannic oxide-tungsten oxide composite sol (this is described in Japanese Patent Laid-Open No. 27301/1994) was used in place of 49 parts by weight of the methanol sol of modified stannic oxide-zirconium oxide composite (this was prepared in Production Example 1) in the step of Example 1(1). Its data are given in Table 1.

Comparative Example 2:

[0097] The same process as in Example 2 was repeated, except that the cured film-coated plastic lens substrate produced in Comparative Example 1 was used in place of that produced in Example 1. The data of the coated lens are given in Table 1.

Comparative Example 3:

[0098] A cured film-coated plastic lens was produced in the same manner as in Example 1, except that 49 parts by weight of a tungsten oxide-stannic oxide composite sol (this is described in Japanese Patent Laid-Open No. 27301/1994) and 10 parts by weight of a silica sol dispersed in methanol (having a particle size of from 10 to 20 nm and a solid content of 20 % by weight) were used in place of 49 parts by weight of the methanol sol of modified stannic oxide-zirconium oxide composite (this was prepared in Production Example 1) in the step of Example 1(1). Its data are given in Table 1.

Comparative Example 4:

[0099] The same process as in Example 2 was repeated, except that the cured film-coated plastic lens substrate produced in Comparative Example 3 was used in place of that produced in Example 1. The data of the coated lens are given in Table 1.

Comparative Example 5:

[0100] A cured film-coated plastic lens was produced in the same manner as in Example 1, except that 49 parts by weight of a silica sol dispersed in methanol (having a particle size of from 10 to 20 nm and a solid content of 20 % by weight) was used in place of 49 parts by weight of the methanol sol of modified stannic oxide-zirconium oxide composite (this was prepared in Production Example 1) in the step of Example 1(1). Its data are given in Table 1.

Comparative Example 6:

[0101] The same process as in Example 2 was repeated, except that the cured film-coated plastic lens substrate produced in Comparative Example 5 was used in place of that produced in Example 1. The data of the coated lens are given in Table 1.

Table 1

	Evaluation of Initial Physical Properties				Evaluation of Physical Properties after Moisture Resistance Test				Evaluation of Physical Properties after Weather Resistance Test			
	Scratch Resistance	Adhesiveness	Interference Fringes	Transparency	Scratch Resistance	Adhesiveness	Interference Fringes	Transparency	Scratch Resistance	Adhesiveness	Interference Fringes	Transparency
Ex. 1	OO	OO	O	O	O	OO	O	O	O	OO	O	O
Ex. 2	OO	OO	O	O	O	OO	O	O	O	OO	O	O
Ex. 3	OO	OO	O	O	O	OO	O	O	O	OO	O	O
Ex. 4	OO	OO	O	O	O	OO	O	O	O	OO	O	O
Ex. 5	OO	OO	O	O	O	OO	O	O	O	OO	O	O
Ex. 6	OO	OO	O	O	O	OO	O	O	O	OO	O	O
Comp.Ex.1	O	OO	O	O	△	OO	O	O	△	OO	O	O
Comp.Ex.2	O	OO	O	O	△	OO	O	O	△	O	O	O
Comp.Ex.3	△	O	O	×	×	△	O	×	×	△	O	×
Comp.Ex.4	△	O	O	×	×	△	O	×	×	△	O	×
Comp.Ex.5	OO	OO	×	O	O	O	×	O	O	O	×	O
Comp.Ex.6	OO	OO	×	O	O	O	×	O	O	O	×	O

[0102] As in Table 1, it is understood that the cured film-coated optical elements of Examples 1 to 6 all have good scratch resistance, good adhesiveness, high transparency, good moisture resistance and good weather resistance,

without having interference fringes. As opposed to these, the cured film-coated optical elements of Comparative Examples 1 and 2 have poor moisture resistance and poor weather resistance; and those of Comparative Examples 3 and 4 have poor scratch resistance, low transparency, poor moisture resistance and poor weather resistance. The cured film-coated optical elements of Comparative Examples 5 and 6 have interference fringes, and their appearances are problematic from the esthetic viewpoint.

[Advantages of the Invention]

[0103] The cured film-coated optical element of the invention has good scratch resistance, good moisture resistance and good weather resistance. Even when a film of an inorganic oxide deposit is formed thereon, the properties of the cured film are degraded little. Even when high-refractive-index plastic lenses are coated with the cured film, they do not have interference fringes.

Claims

1. An optical element comprising an optical substrate and a cured coating film on the optical substrate, wherein the cured coating film is formed of a coating agent which comprises (A) modified stannic oxide-zirconium oxide composite colloid particles as obtainable by coating at least a part of the surfaces of stannic oxide-zirconium oxide composite colloid particles with stannic oxide-tungsten oxide-silicon oxide composite colloid particles, and (B) an organosilicon compound.

2. An optical element according to claim 1 wherein said optical element further comprises an antireflection film of a deposit of an inorganic oxide on the said cured coating film.

3. An optical element according to claim 1 wherein said optical substrate is a plastic lens.

4. An optical element according to claim 1 wherein said optical substrate is a plastic lens having a refractive index of from 1.55 to 1.62.

5. An optical element according to claim 1 wherein said optical substrate is a plastic lens composed of a polythiourethane resin.

6. An optical element according to claim 1 wherein said modified stannic oxide-zirconium oxide composite colloid particles of the component (A) in the coating agent have a particle size of from 4.5 to 60 nm, and are obtainable by coating at least a part of the surfaces of stannic oxide-zirconium oxide composite colloid particles which have a particle size of from 4 to 50 nm and are composed of stannic oxide colloid particles and zirconium oxide colloid particles bonded in a ratio by weight, ZrO_2/SnO_2 falling between 0.02 and 1.0, with tungsten oxide-stannic oxide-silicon dioxide composite colloid particles having a particle size of from 2 to 7 nm and having a ratio by weight, WO_3/SnO_2 and a ratio by weight, SiO_2/SnO_2 each falling between 0.1 and 100.

7. The optical element according to claim 1, wherein said modified stannic oxide-zirconium oxide composite colloid particles of the component (A) in the coating agent are prepared in a process comprising;

   (a) a step of mixing an aqueous stannic oxide sol which contains stannic oxide colloid particles having a particle size of from 4 to 50 nm and having an SnO_2 concentration of from 0.5 to 50 % by weight, with an aqueous solution or suspension of an oxyzirconium salt having a ZrO_2 concentration of from 0.5 to 50 % by weight, in a ratio by weight, ZrO_2/SnO_2 falling between 0.02 and 1.0,
   (b) a step of heating the mixture obtained in the previous step (a) to form an aqueous, stannic oxide-zirconium oxide composite sol having a particle size of from 4 to 50 nm,
   (c) a step of preparing an aqueous solution containing a tungstate, a stannate and a silicate in a ratio by weight, WO_3/SnO_2 and a ratio by weight, SiO_2/SnO_2 each falling between 0.1 and 100, and removing the cations from the aqueous solution to form a tungsten oxide-stannic oxide-silicon dioxide composite sol having a particle size of from 2 to 7 nm,
   (d) a step of mixing the aqueous, stannic oxide-zirconium oxide composite sol prepared in the previous step (b) with the tungsten oxide-stannic oxide-silicon dioxide composite sol prepared in the step (c), in such a ratio that the total of WO_3, SnO_2 and SiO_2 is from 2 to 100 parts by weight relative to 100 parts by weight of the total of ZrO_2 and SnO_2, to form an aqueous, modified stannic oxide-zirconium oxide composite sol having a particle size of from 4.5 to 60 nm, and

(e) a step of contacting the aqueous, modified stannic oxide-zirconium oxide composite sol prepared in the previous step (d) with an anion exchanger to thereby remove the anions from the sol.

8. The optical element according to claim 1, wherein said organosilicon compound of the component (B) in the coating agent is at least one selected from compounds of a general formula (I):

$$R^1_nSi(OR^2)_{4-n} \qquad (I)$$

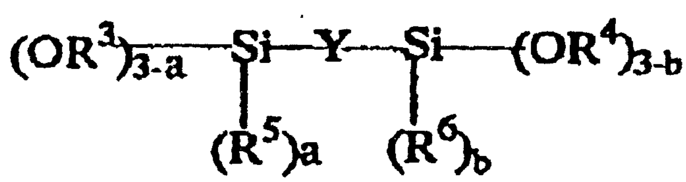
wherein R^1 represents a monovalent hydrocarbon group having from 1 to 20 carbon atoms, and having or not having a functional group; R^2 represents an alkyl, aryl, aralkyl or acyl group having from 1 to 8 carbon atoms; n represents 0, 1 or 2; and plural R^1's, if any, may be the same or different, and plural R^2O's may be the same or different.

and their hydrolyzates.

9. The optical element according to claim 1, wherein said organosilicon compound of the component (B) in the coating agent is γ-glycidoxypropyltrimethoxysilane.

10. The optical element according to claim 1, wherein said organosilicon compound of the component (B) in the coating agent is β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane.

11. The optical element according to claim 1, wherein said organosilicon compound of the component (B) in the coating agent is at least one selected from compounds of a general formula (II):



(II)

wherein R^3 and R^4 each represent an alkyl or acyl group having from 1 to 4 carbon atoms, and may be the same or different; R^5 and R^6 each represent a monovalent hydrocarbon group having from 1 to 5 carbon atoms, and having or not having a functional group, and may be the same or different; Y represents a divalent hydrocarbon group having from 2 to 20 carbon atoms; a and b each represent 0 or 1; and plural OR^3's may be the same or different, and plural OR^4's may be the same or different,

and their hydrolyzates.

12. The optical element according to claim 1, wherein said coating agent further comprises a curing agent.

13. The optical element according to claim 12, wherein said curing agent comprises a metal salt of perchloric acid.

14. The optical element according to claim 13, wherein said metal salt of perchloric acid is aluminium perchlorate.

15. The optical element according to claim 1, wherein said coating agent further comprises water and/or a hydrophilic organic solvent.

16. The optical element according to claim 1, wherein said coating agent contains the colloid particles of the component (A) in a ratio falling between 1 and 500 parts in terms of the solid content relative to 100 parts by weight of the organosilicon compound of the component (B).

17. The optical element according to claim 1, wherein said optical element is a lens.

18. The optical element according to claim 1, wherein said optical element is a lens for glasses or a camera.

19. The optical element according to claim 1, wherein said optical element is a windshield.

20. The optical element according to claim 1, wherein said optical element is an optical filter.

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(54) An optical element having cured coating film

(57) The invention provides a cured film-coated optical element having good scratch resistance, good moisture resistance and good weather resistance, of which the properties are degraded little even when it is further coated with a deposit film of an inorganic oxide. Provided is an optical element having, on an optical substrate, a cured film formed of a coating agent that contains (A) modified stannic oxide-zirconium oxide composite colloid particles as prepared by coating at least a part of the surfaces of stannic oxide-zirconium oxide composite colloid particles with stannic oxide-tungsten oxide-silicon oxide composite colloid particles, and (B) an organosilicon compound.

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EUROPEAN SEARCH REPORT

Application Number
EP 00 10 5928

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Place of search	Date of completion of the search	Examiner
THE HAGUE	12 June 2001	Ward, S

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